

# **ICP-MS Method for Pb and Other Metals in TSP/PM10**

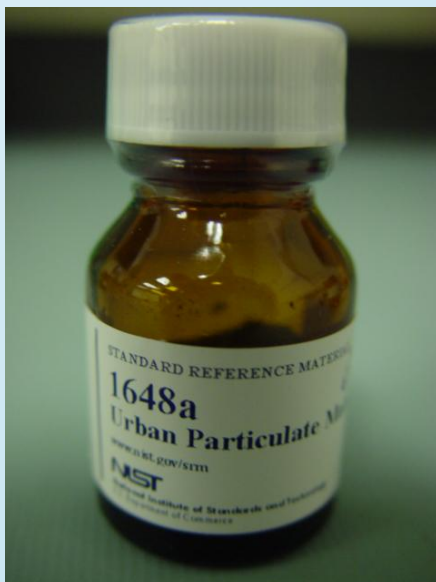
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# Overview of Presentation

- Complexity of sample matrix.
- Data from ERG's experiments with NIST 1648a.
- Improving total metals recoveries for the EPA national contract and NATTS sites using a modified hot acid extraction of the Compendium Method IO-3.1
- Spinel oxides and their recoveries.
- Analytical limitations can impact choice of extraction technique.
- Bio-accessibility of metals in ambient particulate matter (APM).
- The future of APM extraction and analysis.
- Conclusions

# Sample Matrix Complexity



National Institute of Standards & Technology

## Certificate of Analysis

Standard Reference Material® 1648a  
Urban Particulate Matter

Standard Reference Material (SRM) 1648a is an atmospheric particulate matter collected in an urban area and is intended primarily for use as a control material and in the evaluation of methods used in the inorganic analysis of atmospheric particulate matter and materials with similar matrix. All constituents for which certified, reference, and information values are provided in SRM 1648a were naturally present in the material before processing. While not represented to be typical of the area where it was collected nor of contemporary composition of an urban aerosol, its use should typify the analytical problems of atmospheric particulate samples obtained from industrialized urban areas. SRM 1648a is the same particulate material that has been issued previously in 1978 as SRM 1648; the material has been re-batched, tested, and reanalyzed to provide updated certified values, reference values, and information data based on a more typically used milligram size sample. A unit of SRM 1648a consists of one bottle containing 2 g of atmospheric particulate matter.

**Certified Values:** Certified values, expressed as mass fractions, for the content of 24 elements are provided in Table 1. The certified values are based on the agreement of results from two or more chemically independent analytical techniques obtained at NIST and collaborating expert laboratories [1]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

**Reference Values:** Reference values, expressed as mass fractions, are provided for the content of eight additional elements in Table 2. Reference values are non-certified values that are the best estimate of the true value. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1].

**Information Values:** Information values, expressed as mass fractions, are provided in Table 3 for the content of six elements. An information value is considered to be a value that will be of interest and use to the SRM user, but for which insufficient information is available to assess adequately the uncertainty associated with the value, or a value derived from a limited number of analyses [1].

**Expiration of Certification:** The certification of SRM 1648a is valid, within the measurement uncertainties specified, until 31 October 2027, provided the SRM is handled and stored in accordance with the instructions given in the certificate (see "Notice and Warnings to Users"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

**Maintenance of SRM Certification:** NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The coordination of the investigatory and technical measurements leading to the certification of this material was under the leadership of R. Zoller of the NIST Analytical Chemistry Division.

Consultation on the statistical design of the experimental work and evaluation of the data were provided by S.D. Leigh of the NIST Statistical Engineering Division.

Stephen A. Wise, Chief  
Analytical Chemistry Division

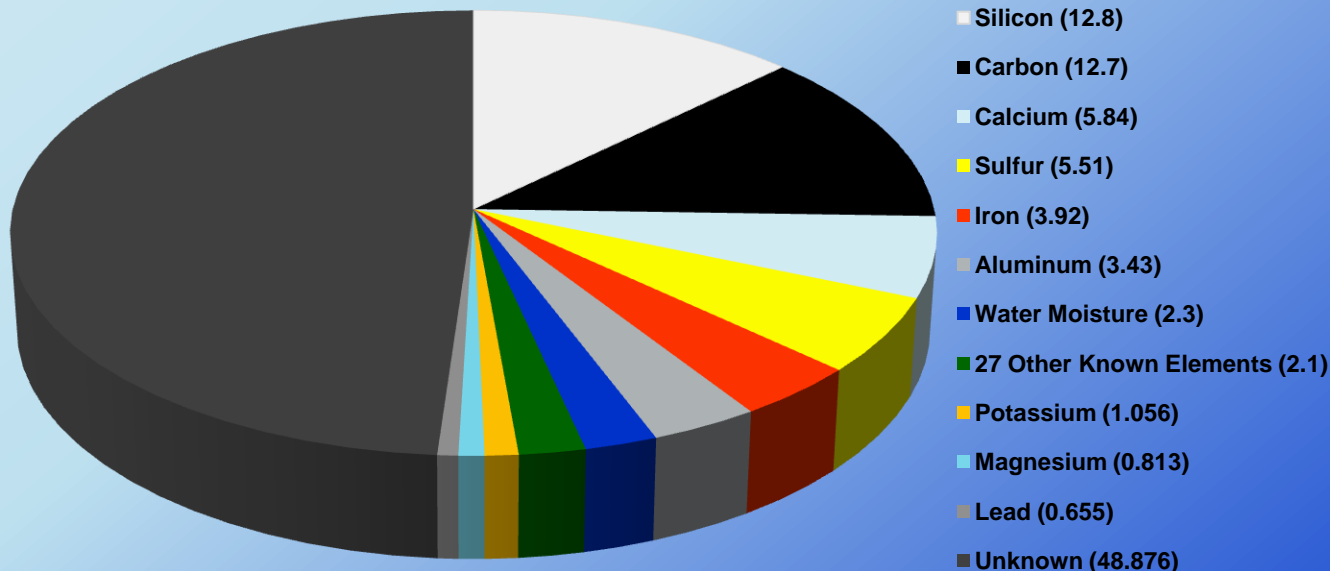
Robert L. Waters, Jr., Chief  
Measurement Services Division

Gaithersburg, MD 20899  
Certificate Issue Date: 08 April 2008

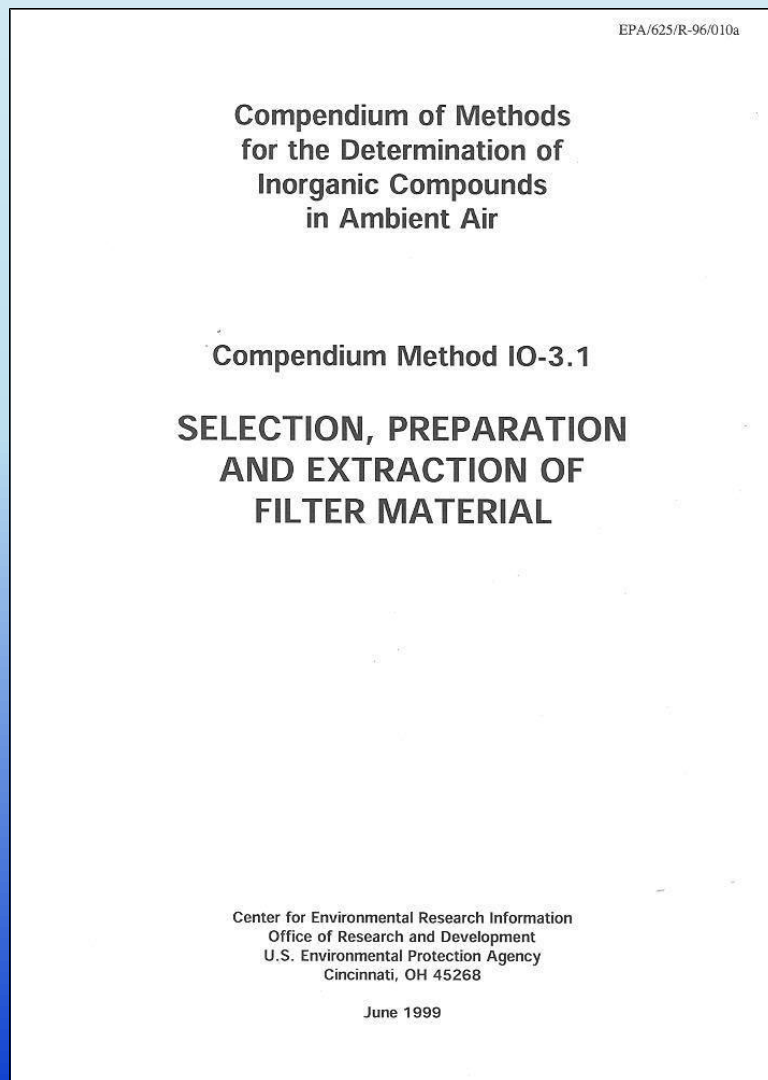
SRM 1648a

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## Percent Composition of the National Institute of Standards & Temperature (NIST) 1648a



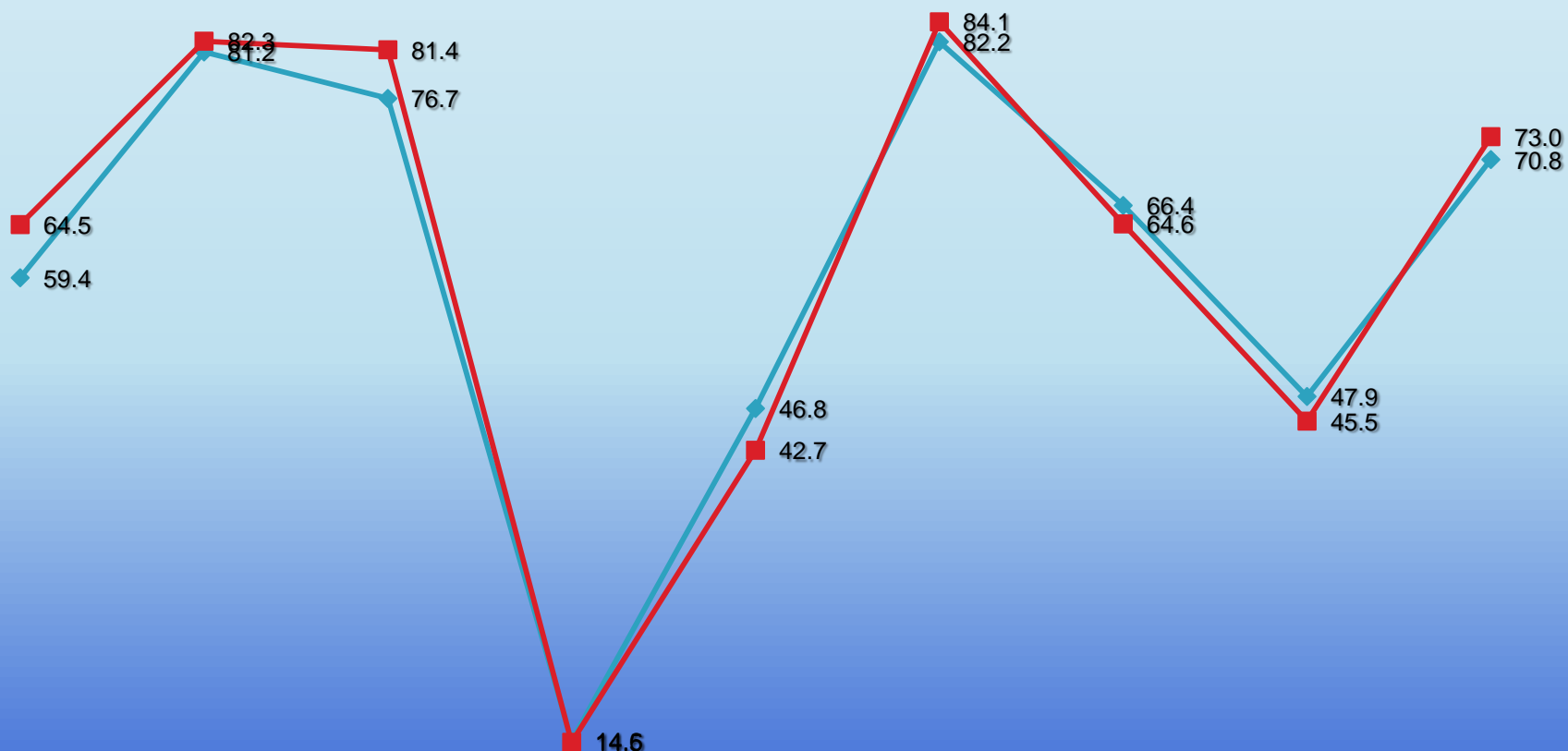
# Improving the Hot Acid Extraction of the Compendium Method IO-3.1



## NIST 1648a Percent Recoveries for HotBlock™ and Ultrasonication Method

—◆— HB 0.5 mg in 5% HNO<sub>3</sub> for 1 hr. 20 min. %Rec. (n = 4)

—■— UE 0.5 mg in 4% HNO<sub>3</sub> for 3 hr. Rec. (n = 4)



Antimony

Arsenic

Cadmium

Chromium

Cobalt

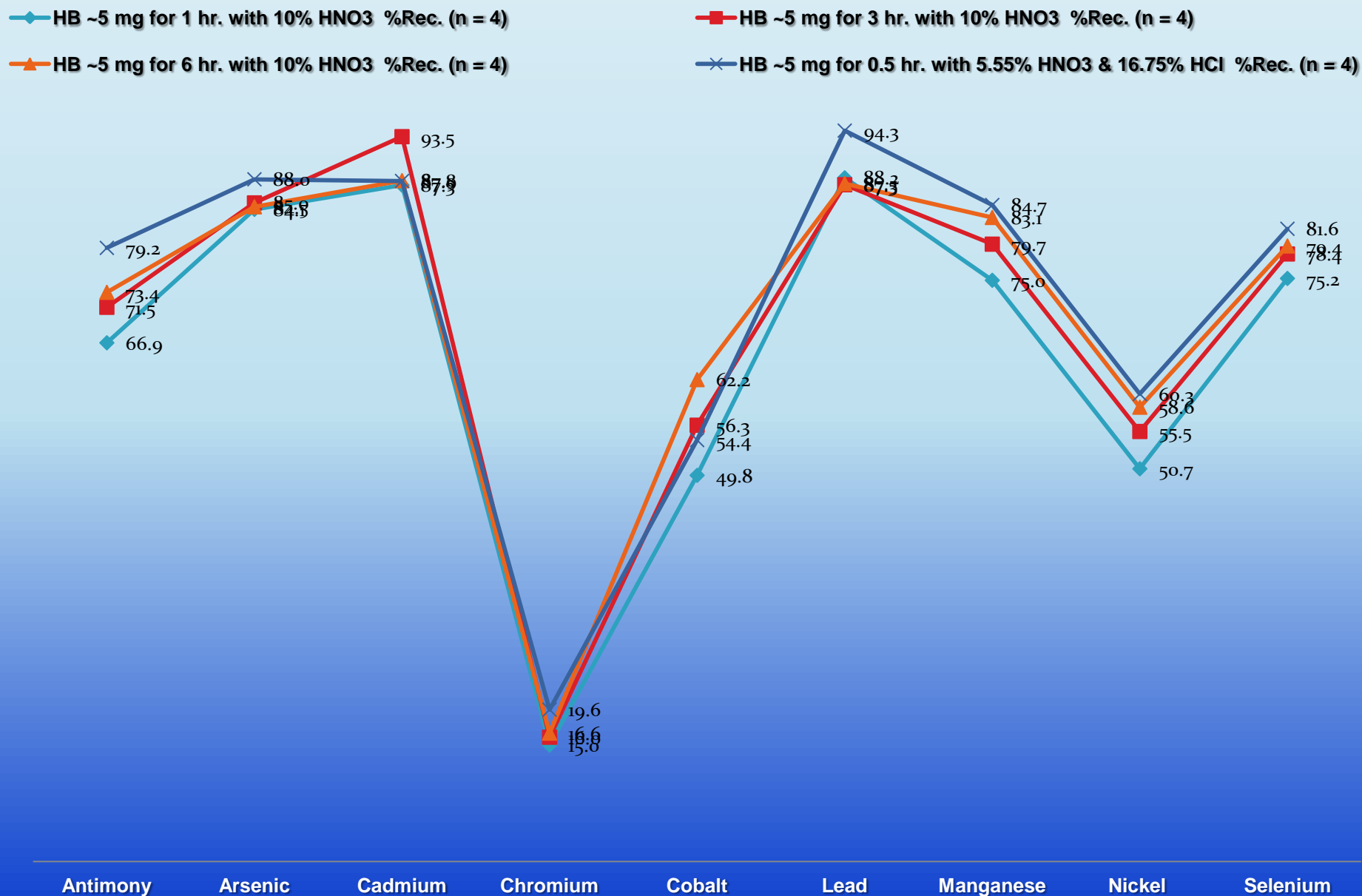
Lead

Manganese

Nickel

Selenium

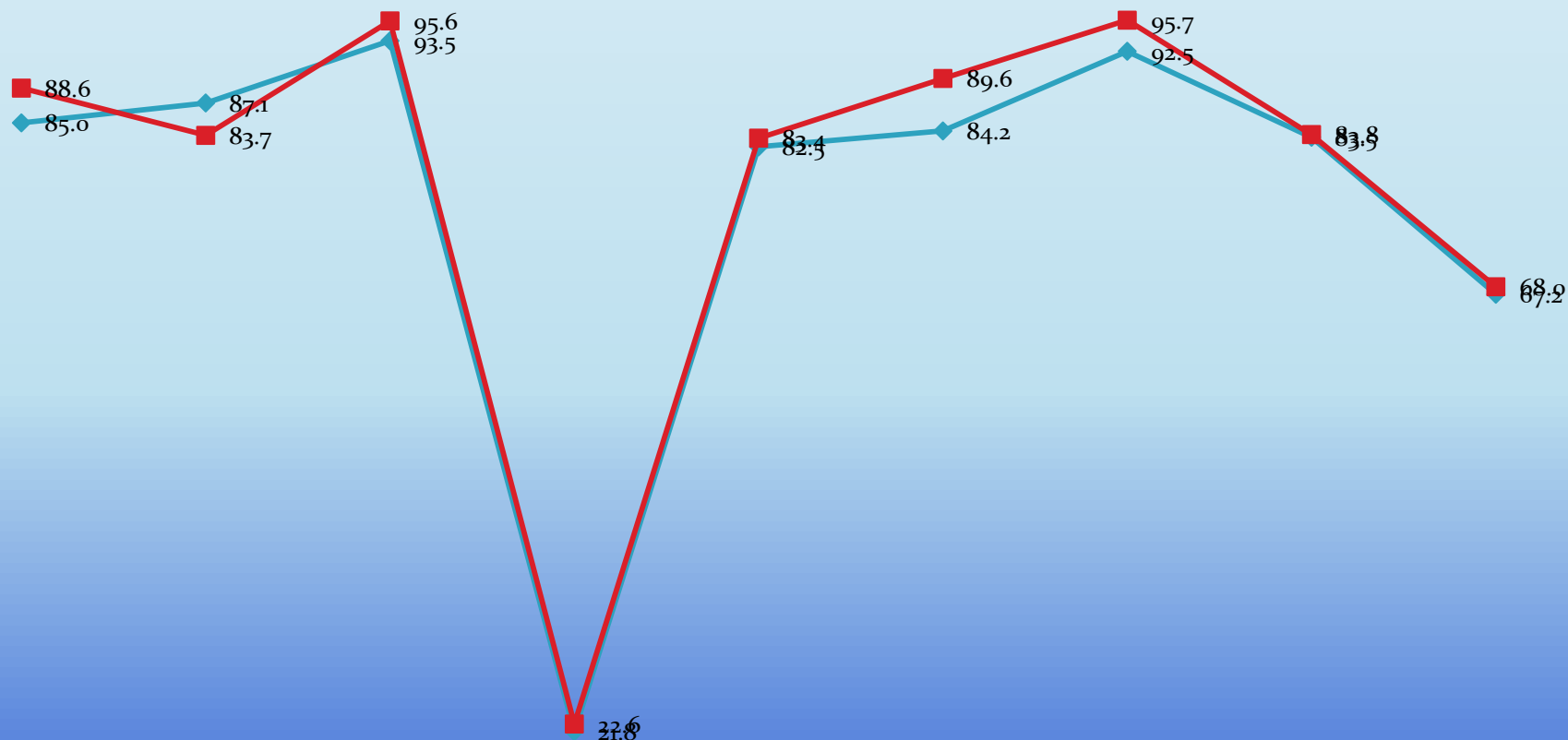
# NIST 1648a Recoveries for 10% Nitric vs IO3.1 Method



## Modified IO3.1 with H<sub>2</sub>O<sub>2</sub> and/or HF

—◆ NIST ~ 5-7 mg for 3 hr. HB with 0.5% HF 5.55% HNO<sub>3</sub> 16.75% HCl % Rec. (n = 4)

—■ NIST ~ 5-7 mg for 2.5 hr. HB with 0.5% HF 5.55% HNO<sub>3</sub> 16.75% HCl & H<sub>2</sub>O<sub>2</sub> % Rec. (n = 4)



Antimony

Arsenic

Cadmium

Chromium

Cobalt

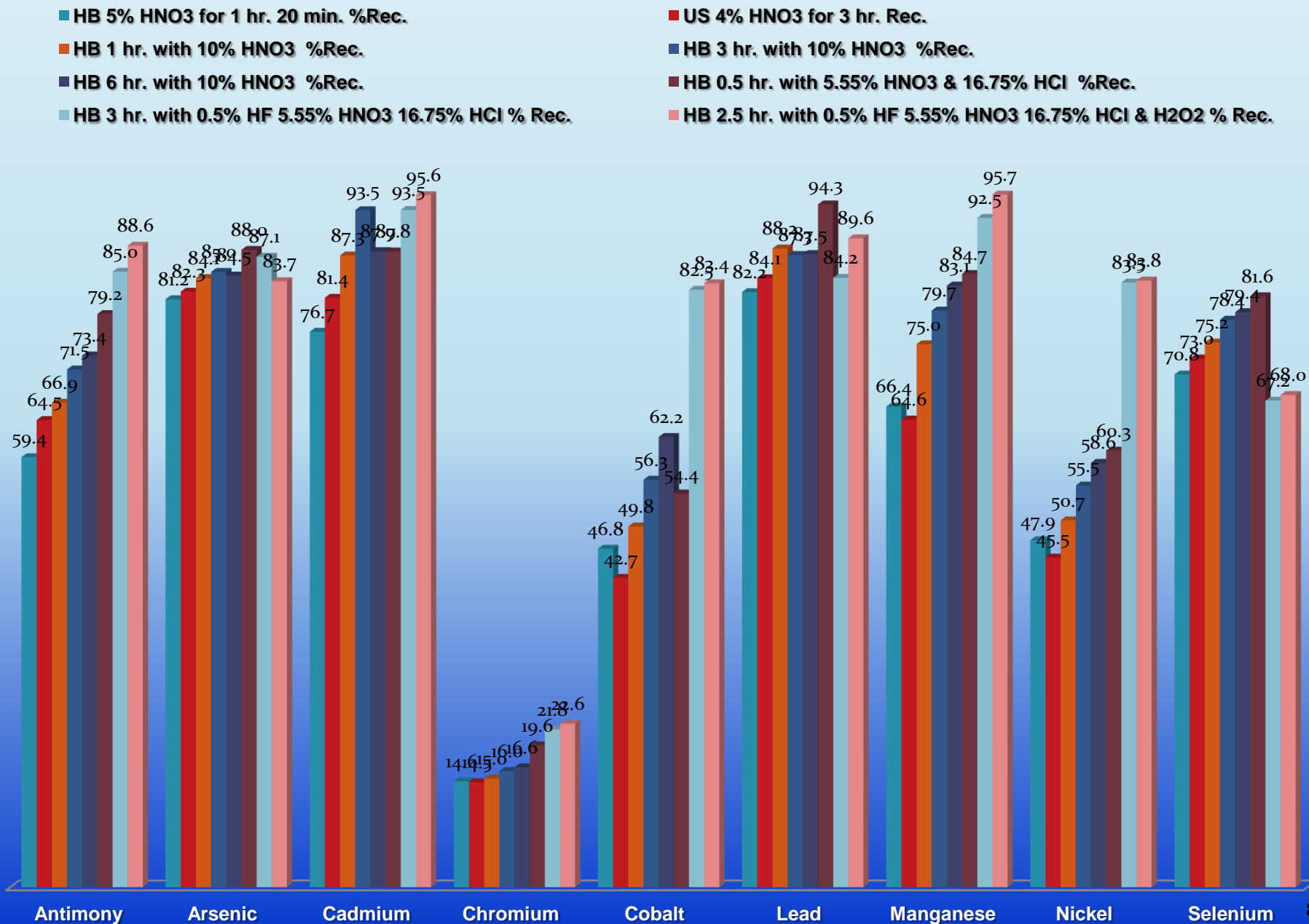
Lead

Manganese

Nickel

Selenium

# Comparison of **ERG** Method Development Results

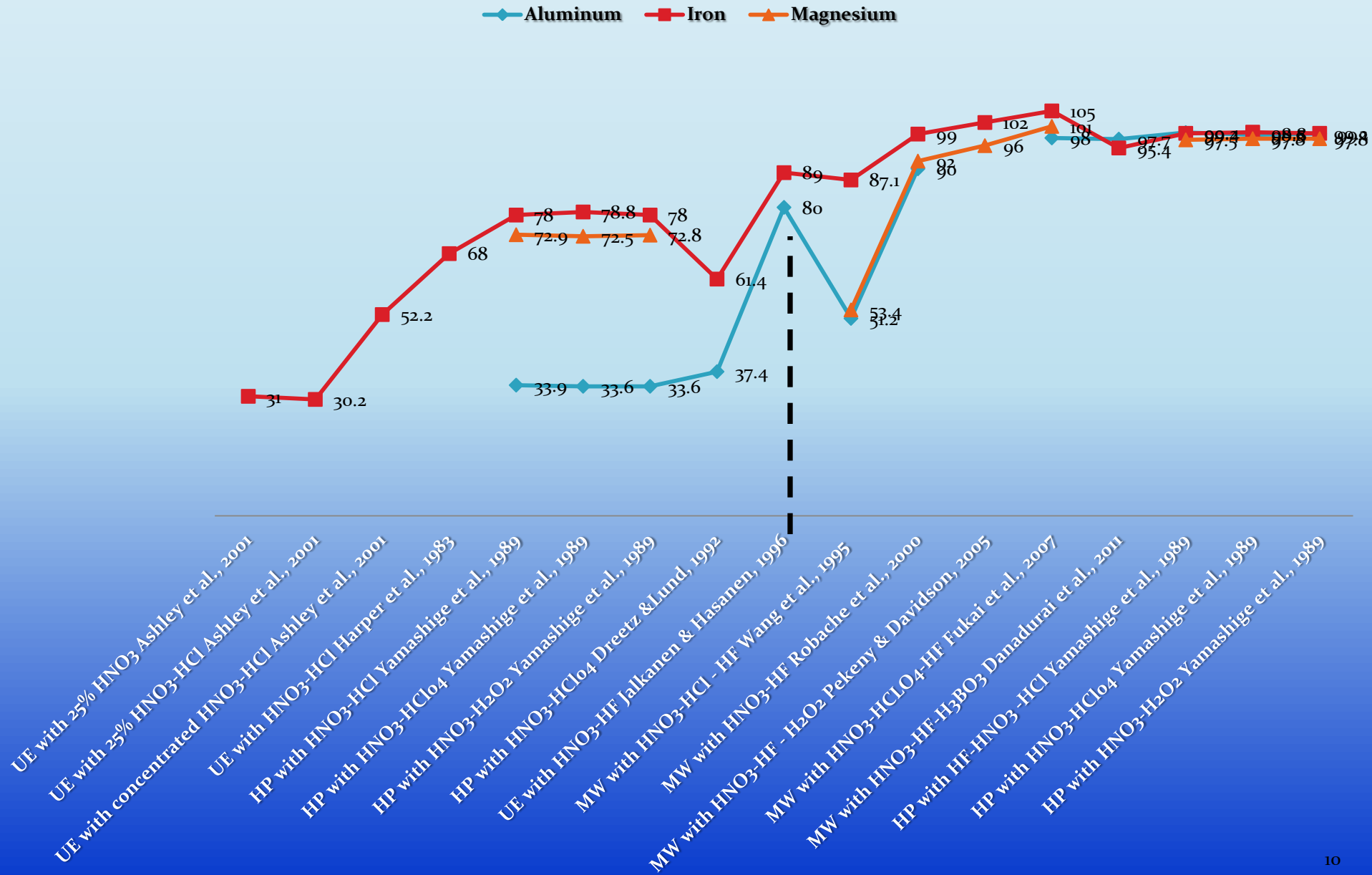




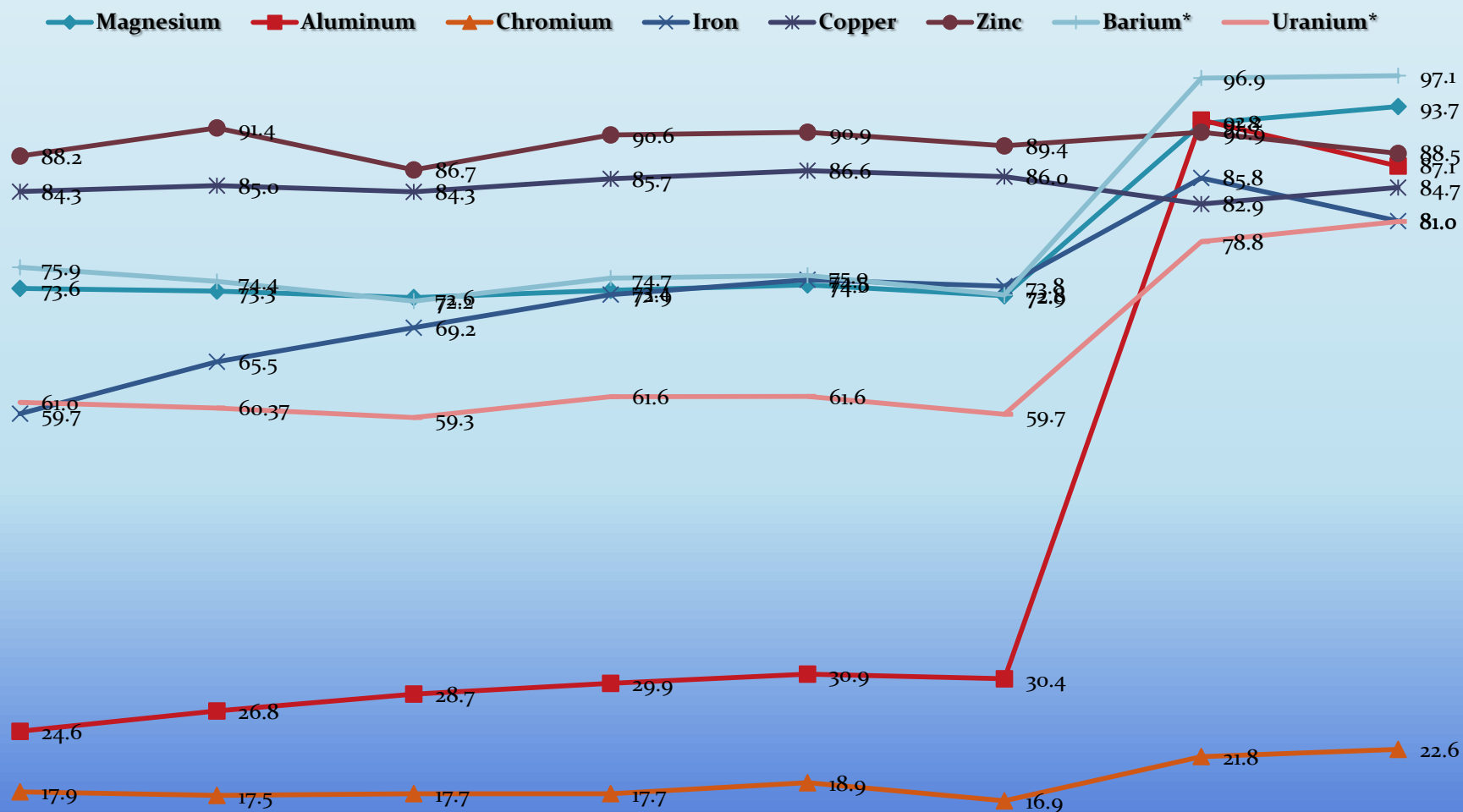
# Spinel Oxides and the Problems of Getting Elements Associated with them Out of APM

- Many elements that are in PM are bound in spinel oxides (see Butler & Howe, 1999 and Yamashige, et al., 1989), which are in the general chemical formula of  $A^{2+}B_2^{3+}O_4^{2-}$ .
- The A and B cations are elements like Mg, Al, Cr, Mn, Fe, Co, Ni, Cu and Zn.
- For example: an aluminum spinel  $MgAl_2O_4$ ,  $FeCr_2O_4$  known as chromite, or ilmenite as  $FeTiO_3$ .
- Chromium can not only be a component of spinel oxides but it can form insoluble oxides under acid conditions (see Ashley et al., 2001 and references therein).
- These elements associated with spinel oxides have proven to be difficult to extract through conventional means and in particular Cr has a long history of being difficult.
- The reason for this is that these spinel oxides are refractory – meaning: difficult to fuse, corrode, or draw out; *especially*: capable of enduring high temperature (definition from Merriam-Webster dictionary).
- These refractory compounds have demonstrated their resistance to even concentrated acids such as  $HNO_3$ ,  $HCl$  and even  $HF$  (see Butler & Howe, 1999; Jalkanen & Häsänen, 1996 and Yamashige, et al., 1989).
- One study suggested that the difficulty of extracting Cr was due to the soot content or organic material (see Jalkanen and Häsänen, 1996).

# Comparison of Major Spinel Element Recoveries from Literature



# Improved Recoveries of Spinel and Other Elements in NIST 1648a with H<sub>2</sub>O<sub>2</sub> and/or HF



\*The values for these elements are not included with NIST 1648a; the barium reference value taken from Yamashige et al., 1989 and the uranium value was taken from a study done at Iowa State University in 2005 (see: <http://www.osti.gov/bridge/servlets/purl/882989-wfWShW/882989.pdf>)

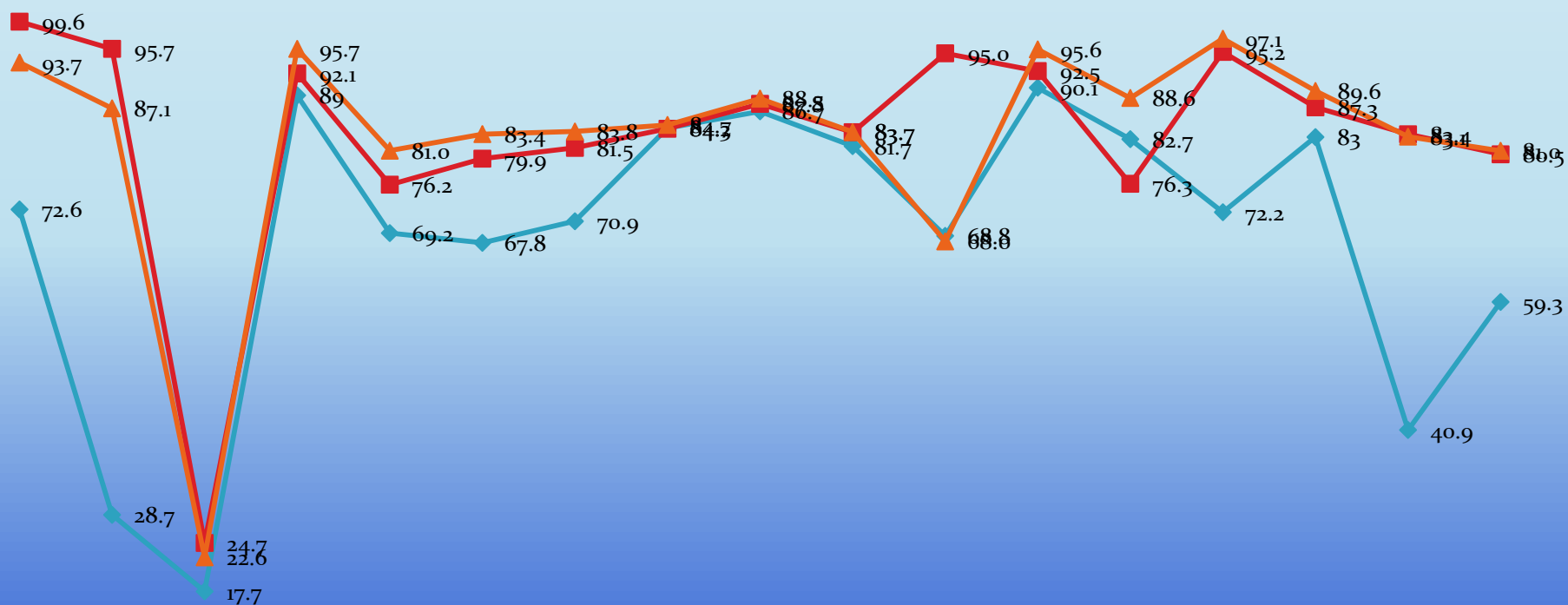
HB 1 hr. IO3.1 (n = 1) HB 2 hr. IO3.1 (n = 1) HB 3 hr. IO3.1 (n = 1) HB 3.5 hr. IO3.1 (n = 1) HB 4 hr. IO3.1 (n = 1) HB 4.5 hr. IO3.1 (n = 1) HB 3 hr. IO3.1 + 0.5% HF (n = 4) HB 2.5 hr. IO3.1 + 0.5% HF & H<sub>2</sub>O<sub>2</sub> (n = 4)

## Comparison of IO-3.1 to UE with HF and HB with HF and H<sub>2</sub>O<sub>2</sub>

— HB 3 hr. IO-3.1, 16.75% HCl & 5.55% HNO<sub>3</sub> (n=1)

— UE 3 hr. 0.5% HF, 16.75% HCl & 5.55% HNO<sub>3</sub> (n=4)

— HB 3 hr. 0.5% HF, 16.75% HCl & 5.55% HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> (n=4)



\*The values for these elements are not included with NIST 1648a; the barium reference value taken from Yamashige et al., 1989 and the uranium value was taken from a study done at Iowa State University in 2005 (see: <http://www.osti.gov/bridge/servlets/purl/882989-wfWShW/882989.pdf>)

# Analytical Limitations Impact Extraction

- After establishing an improved method of extracting NIST 1648a some analytical limitations were discovered.
- NIST 1648a samples were initially extracted without matrix of quartz or Teflon filters.
- An ELAN 9000 ICP-MS that does not have a DRC was used for all analytical determinations.
  - With the quartz filter extracted using HF an unknown matrix interference was created causing the lower mass internal standards to recover poorly, which may be due to the high [Si] or maybe  $\text{SiF}_6$ .
  - A final concentration of 3.35% HCl in the extract proved difficult to maintain acceptable MDL's for As and Se.

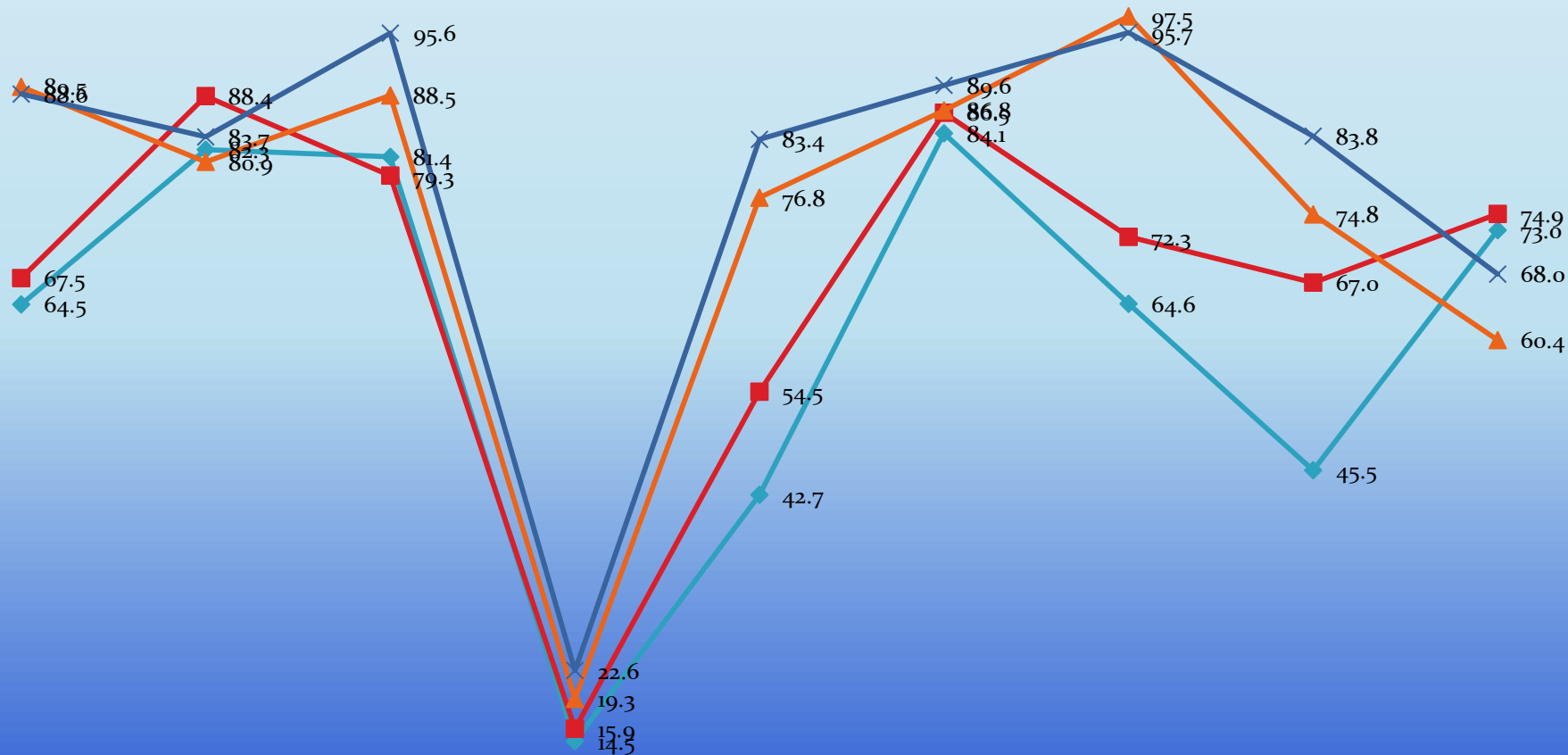


# Reasons and Resolutions for Analytical Limitations

- An ICP-MS without DRC or CCT cannot eliminate polyatomic interferences and instead are handled with tune conditions and correction equations.
  - (i.e.  $40\text{Ar} + 35\text{Cl}$  interferes with  $75\text{As}$ )
- Large quantities of  $40\text{Ar}35\text{Cl}$  creates a relatively more unstable background making MDLs higher.
  - Decreased  $[\text{HCl}]$  until As MDL was acceptable.
- The large quantity of Si in the extracts of quartz filters with HF could cause a physical interference great enough to have low internal standard recoveries.
  - Removed HF from Quartz extractions.
  - Future experiments may find a way to eliminate this problem.

# Comparison of Old, Current and “Best” Extraction Methods

- US 3 hr. 4% HNO3 Old Method
- HB 2.5 hr. 1.5% HCl 5.55% HNO3 + H2O2 Current Quartz Extraction Method
- HB 2.5 hr. 0.17% HF 0.5% HCl 1.85% HNO3 + H2O2 Current Teflon Extraction Method
- HB 2.5 hr. with 0.5% HF 5.55% HNO3 16.75% HCl & H2O2 "Best" Method



Antimony

Arsenic

Cadmium

Chromium

Cobalt

Lead

Manganese

Nickel

Selenium

## ERG's Expansion of Elements for Analysis

- Aluminum
- Barium
- Copper
- Iron\*
- Magnesium\*
- Molybdenum
- Rubidium\*
- Strontium\*
- Thallium
- Thorium
- Uranium
- Zinc

**\* Elements not listed in the IO-3.5 Method that could also be used for source apportionment studies.**



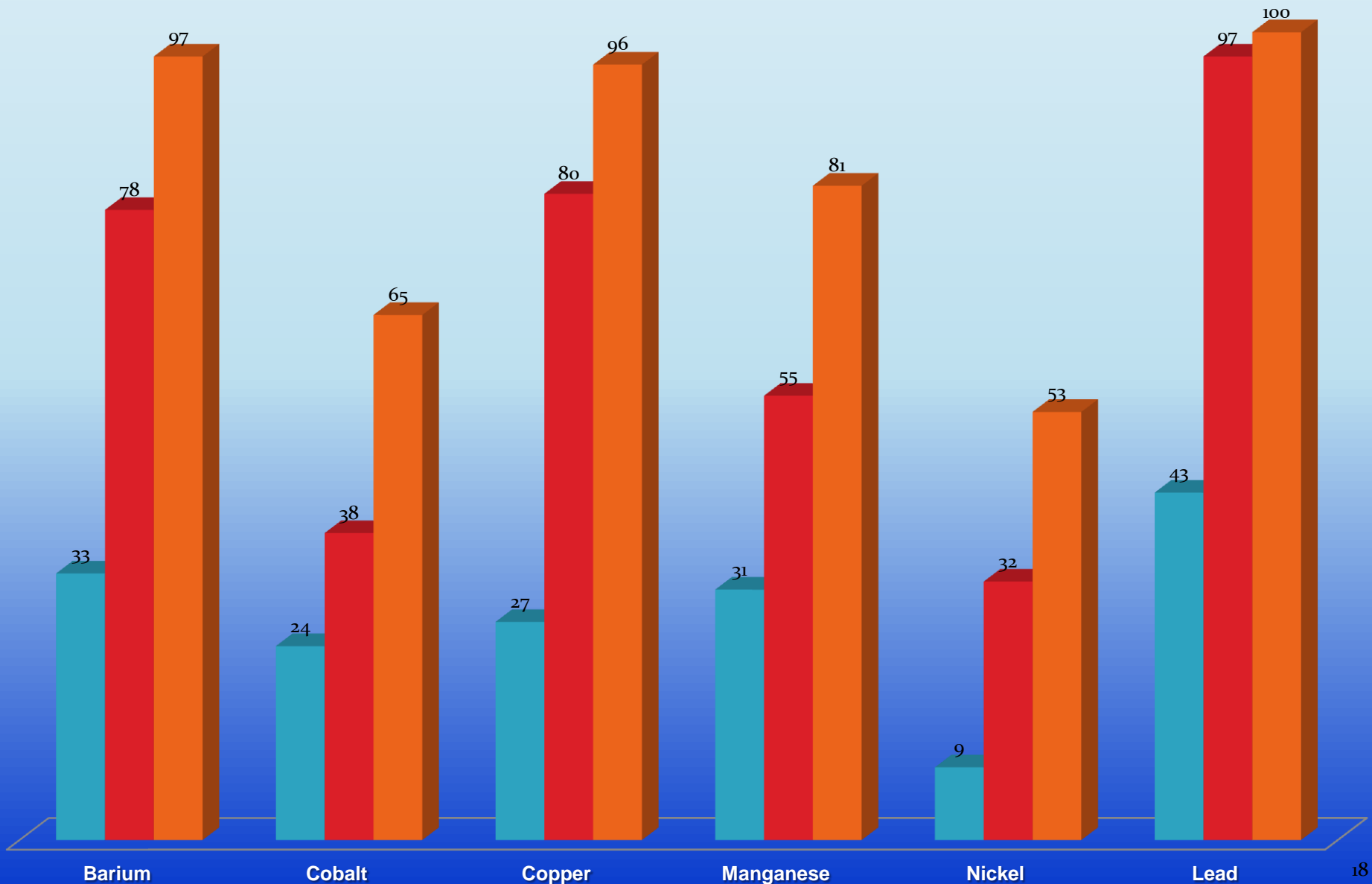
## IO-3.5 Method Development – Pb TSP FEM Approval

- Because of the new NAAQS rule for lead (2008), ERG has proposed a new FEM for analysis by ICP-MS.
  - Reagents used:
    - $\text{HNO}_3$
    - $\text{HCl}$
    - $\text{HF}$
    - $\text{H}_2\text{O}_2$
  - HotBlock™ (not ultrasonic extraction)
  - Recoveries for NIST 1648a Pb with new method ~90%.
  - With the use of the additional acids this method also provides improved data for other elements of the EPA national contract and NATTS sites.

# Range and Mean of Bio-accessible Trace Metals Fractions from Mukhtar & Limbeck, 2011



■ Low Range Bio-accessibility (%)   ■ Mean Bio-accessible (%)   ■ High Range Bio-accessibility (%)



# The Future of APM Analysis

- Do we really want a total digestion of the sample for total elemental concentrations or are we really interested in bio-accessible trace metal fractions as studied by Mukhtar and Limbeck, 2011?
  - The answer to this question probably depends on the end use of the data.
- If it's only the bio-accessible composition then the remaining undigested APM is perhaps more of a physical concern and not necessarily the total elemental composition.
- For the purpose of source apportionment studies it may be best to completely digest the APM.

# Conclusions

- Lead is not difficult to extract from APM but many other metals are and the recovery of lead may be impacted when attempting multi-element extractions using an ultrasonic bath or HotBlock™.
- The extraction procedure chosen to analyze APM is dependent upon which elements are more important for data end use.
- Other types of extraction techniques such as microwave and alkali fusion may prove to be the favored methods of the future when total elemental concentrations are required.
- Risk assessment of metal toxicity should focus on bio-accessible concentrations and not total concentrations.
- Bio-accessible concentrations are best obtained through dissolution techniques like those described in this study utilizing ultrasonication or HotBlocks™ because techniques and instrumentation used for total elemental concentrations cannot quantitate bio-accessible metals.
- The literature and ERG experiments of NIST 1648(a) demonstrate that while total recoveries for certain metals are best with some methods you may negatively impact the recovery of other metals.
- We were able to improve upon our UE method by modifying the acid concentrations and switching to a HotBlock™, which improved total recoveries of many metals in APM.

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  - Kerry Fountain – PowerPoint assistance.
  - Randy Mercurio – photographs unless otherwise noted.